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Thermodynamic analysis of hydrogen production via sorption-enhanced steam methane reforming in a new class of variable volume batch-membrane reactor

David M. Anderson^a, Peter A. Kottke^a, Andrei G. Fedorov^{a,b,*}^a G.W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA^b Parker H. Petit Institute of Bioengineering and Bioscience, Georgia Institute of Technology, Atlanta, GA 30332, USA

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ABSTRACT

Combined reaction–separation processes are a widely explored method to produce hydrogen from endothermic steam reforming of hydrocarbon feedstock at a reduced reaction temperature and with fewer unit operation steps, both of which are key requirements for energy efficient, distributed hydrogen production. This work introduces a new class of variable volume batch reactors for production of hydrogen from catalytic steam reforming of methane that operates in a cycle similar to that of an internal combustion engine. It incorporates a CO₂ adsorbent and a selectively permeable hydrogen membrane for *in situ* removal of the two major products of the reversible steam methane reforming reaction. Thermodynamic analysis is employed to define an envelope of ideal reactor performance and to explore the tradeoff between thermal efficiency and hydrogen yield density with respect to critical operating parameters, including sorbent mass, steam to methane ratio and fraction of product gas recycled. Particular attention is paid to contrasting the variable volume batch-membrane reactor approach to a conventional fixed bed reaction–separation approach. The results indicates that the proposed reactor is a viable option for low temperature distributed production of hydrogen from methane, the primary component of natural gas feedstock, motivating a detailed study of reaction/adsorption kinetics and heat/mass transfer effects.

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Introduction

Natural gas has recently been touted as a bridge fuel to a low-carbon future because of its favorable hydrogen-to-carbon ratio and newly developed techniques to tap vast, previously

inaccessible worldwide reserves [1,2]. With its newfound abundance, additional methods of natural gas utilization are desirable, including approaches for efficient production of hydrogen in a small-scale, distributed fashion at the point of use. Distributed hydrogen production helps overcome one of the primary barriers to the implementation of a so-called

* Corresponding author. G.W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA.

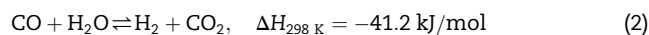
E-mail address: AGF@gatech.edu (A.G. Fedorov).

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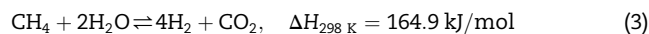
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“hydrogen economy”: the lack of a large-scale hydrogen delivery infrastructure [3]. Active areas of hydrogen research include production, distribution, storage and energy conversion through fuel cells; advances in all of which are necessary to fully realize the benefits of a hydrogen economy [4–8]. Owing to the challenges associated with its distribution, presently 95% of worldwide hydrogen production is captive (i.e., collocated production and usage) [9]. Implementation of efficient small-scale hydrogen production facilities from methane, the primary component of natural gas, at the point of use would allow extension of the captive production strategy to industrial/residential co-generation [10,11] and on-vehicle [12] applications. To understand the challenges associated with this strategy, it is instructive to first briefly discuss the established large-scale industrial processes and consider the difficulties of scaling-down a similar approach for distributed hydrogen production.

Steam methane reforming (SMR) is an industrially mature technology that is the primary route of hydrogen production worldwide from natural gas, accounting for 95% of the hydrogen produced in the United States [13,14]. The SMR process consists of the strongly endothermic reverse methanation reaction, Eq. (1), and moderately exothermic water gas shift (WGS) reaction, Eq. (2):



The combined reaction is endothermic and stoichiometrically defines the maximum H_2 yield for a given quantity of CH_4 :



Reactions (1)–(3) occur in parallel, typically over a nickel catalyst [15]. Because reverse methanation is endothermic while the WGS reaction is exothermic and both reactions are equilibrium limited for typical reactor conditions, it is impossible to achieve complete conversion of CH_4 into CO_2 and H_2 in a single stage of a conventional continuous flow reactor [16]. To shift the equilibrium of the strongly endothermic reverse methanation reaction in a favorable direction of greater hydrogen yield, large-scale industrial steam reformers utilize an initial reactor stage that operates at a highly elevated temperature in a range of 800–900 °C. The reformer is also fed with excess of steam (H_2O), i.e., a high steam to carbon (S/C) molar ratio, to promote further CH_4 conversion and to minimize catalyst coking. While the stoichiometry of the combined reaction, given by Eq. (3), requires an S/C ratio of only 2, industrial SMR processes typically operate at an S/C ratio of between 3 and 6.

Because of the high operating temperature of the initial SMR reactor stage, which is thermodynamically unfavorable for conversion of CO to CO_2 via the exothermic WGS reaction, the effluent gas from a single stage reactor typically contains an unacceptably large amount of CO (8–10% on a dry basis) [13,14]. To substantially reduce the CO concentration and to produce additional H_2 , one or two subsequent low temperature reactors are utilized with conditions favorable for the exothermic WGS reaction. For applications where extremely

pure hydrogen is required, such as PEM fuel cells where CO concentrations above 20 ppm can poison the Pt catalyst [17], additional product purification of residual carbon monoxide from the effluent of the low temperature WGS reactor is achieved via pressure swing adsorption (PSA), membrane separation, or catalytic fine cleanup by preferential oxidation. With numerous sequential unit operations, including intermediate heat exchangers for thermal management of the reagent/product streams between active (reaction/separation) units, as well as a need for high temperature operating conditions, it is clear that industrial SMR is capital intensive, technologically complex and challenging, and requires a large footprint; yet, it is currently the most cost-effective method of commercial scale hydrogen production [3].

On-site, localized production of hydrogen from methane at lower (and dynamically variable) throughputs, which can be used in conjunction with the current natural gas distribution infrastructure, places stringent demand on the complexity/cost, energy (thermal) efficiency and footprint of the fuel processing strategy. Straight-forward miniaturization of the conventional industrial approach is challenging because of the excessive operating temperature (with associated cost and thermal efficiency penalty) and at best linear footprint reduction with production capacity for multi-unit equipment (with possible “non-scalable” component bottlenecks). Thus, to effectively implement SMR processes in smaller-scale distributed applications, the following process attributes are favorable for scale down:

- Lower operating temperature to reduce material cost and preheating energy requirements;
- Multi-functional components (e.g., combined reaction/separation step, elimination of dedicated low temperature WGS reactors) to reduce the overall system complexity and footprint;
- Operation at lower S/C ratio to improve thermal efficiency, to increase volumetric H_2 yield density, and to avoid use of excess steam, which may not be as readily available as it would be in a large-scale industrial plant.

Combined reaction–separation processes are an attractive means to reduce the required SMR operating temperature and increase the practicality of on-site hydrogen generation [18,19]. By Le Chatelier’s principle, selective removal of H_2 and/or CO_2 from the reactor shifts equilibrium toward greater fuel conversion and H_2 yield, thereby circumventing the thermodynamic equilibrium limitations of the SMR process. This results in a suitable level of conversion that can be achieved at much lower temperature, and even potential removal of subsequent WGS and PSA purification steps. Moreover, the *in situ* removal of the reversible reactions’ products enhances the forward reaction kinetics by increasing instantaneous concentrations of the reagents, which can further reduce the required reactor volume for a given H_2 yield, thus increasing the power density. Two SMR reaction–separation processes that have been extensively investigated are packed-bed catalytic H_2 membrane reactors [20–23] and CO_2 sorption-enhanced reactors [11,24–31]. Reactors incorporating CO_2 sorption, termed SE-SMR, produce an improvement in CH_4

conversion at temperatures below 500 °C; however, high S/C ratios (and thus large quantities of readily available steam) are required to achieve suitably high conversion and catalyst stability. As previously described, operating at a high S/C ratio is undesirable for distributed applications. Relatively little attention has been paid to reactor systems that incorporate combined H₂ membrane separation and *in situ* CO₂ sorption, with the exception of the work of Harale et al. [32,33].

The CO₂/H₂ Active Membrane Piston (CHAMP) concept is a variable volume batch-membrane reactor recently proposed for hydrogen production via steam reforming of hydrocarbons [34,35]. The CHAMP operates in a cycle similar to the Internal Combustion (IC) engine, aiming to dynamically maintain the optimal conditions (pressure, temperature, and residence time) for (1) transport of reactants to the catalyst, (2) reaction kinetics at the catalyst, and (3) selective permeation of H₂ through a membrane. In particular, to counteract the effects of fuel depletion and reduction in reactor pressure due to permeation, strategic compression of the CHAMP reactor volume is utilized to increase the concentration of the remaining fuel and hydrogen, thereby providing additional driving force for reaction and permeation. Initial studies of the CHAMP reactor, utilizing methanol as a potential on-vehicle feedstock, demonstrated advantageous performance as compared to a traditional packed-bed continuous flow reactor in terms of the CHAMP's ability to overcome heat and mass transport limitations as well as to match transient H₂ product yield with its demand without sacrificing conversion or yield efficiency [34,35].

The key contribution of this work is to investigate the use of methane as a feedstock in a CHAMP reactor, and to include selective CO₂ sorption to complement the membrane H₂ separation as part of the multi-functional fuel processing strategy to further enhance reactor performance. The remaining of this paper organized as follows. The CO₂/H₂ separation requirements for low temperature SMR section explores the H₂ and CO₂ separation requirements to achieve desired conversion of CH₄ at low temperature. One of most important findings is that conversion above 90% at a temperature as low

as 400 °C and low S/C ratios can only be achieved through a combination of both H₂ membrane separation and CO₂ removal by sorption. This is in contrast to the previous CHAMP studies involving methanol, where full conversion at low temperatures was possible with a hydrogen membrane alone because the methanol–steam reforming reaction is much less endothermic. The CHAMP reactor with CO₂ sorption section then describes how the CHAMP concept can be extended to include CO₂ sorption into a new reactor design termed CHAMP-SORB. Also in this section, desired sorbent characteristics and their impact on the CHAMP-SORB reactor performance are discussed. Lastly, the Results and discussion section introduces a thermodynamic framework for calculating the thermal efficiency of the entire CHAMP-SORB cycle. This section also reports the results of the energy efficiency analysis as function of the key process variables (pressure, temperature, S/C ratio, and sorbent mass), including the possibility of regenerative fuel processing to further increase the fuel conversion. The results are summarized in terms of regime maps for CHAMP-SORB operation, which can be effectively used as design tools for the matching the capabilities of the CHAMP-SORB cycle to the desired application requirements.

CO₂/H₂ separation requirements for low temperature SMR

Before considering a specific design of CHAMP class reactor that can achieve low temperature SMR with *in situ* separation of reaction products, it is useful to first investigate the degree of separation required to achieve high CH₄ conversion at low temperature in a general sense (i.e., without consideration of reactor type). During a combined reaction/permeation/adsorption process, the initial number of moles of each species *j*, N_j^0 , evolves to a final value N_j according to species conservation:

$$N_j = N_j^0 + (1 - r_j) \sum_i \epsilon_i \nu_{ij} - N_{j,perm} \quad (4)$$

where r_j is the fraction of produced species *j* that is adsorbed from the gas phase of the reactor, ϵ_i is the extent of reaction *i*, ν_{ij} is the stoichiometric coefficient of the *j*th component of reaction *i*, and $N_{j,perm}$ is the number of moles of species *j* that permeates out from the reactor. The parameter r_j is non-zero for *j* = CO₂ only when considering CO₂ sorption, while the parameter $N_{j,perm}$ is non-zero for *j* = H₂ only for the case of hydrogen removal through membrane separation. Specifying zero permeation of all non-hydrogen species implies use of a membrane that is infinitely selective to hydrogen, such as palladium-based membranes that have been utilized in previous CHAMP studies [34,35].

If the reactions proceed to equilibrium, the reverse methanation, Eq. (1), and water gas shift, Eq. (2), reactions must satisfy the following constraints:

$$K_1(T) = \frac{y_{H_2}^3 y_{CO}}{y_{CH_4} y_{H_2O}} \cdot \left[\frac{P_{rxn}}{P_{ref}} \right]^2 \quad (5)$$

$$K_2(T) = \frac{y_{H_2} y_{CO_2}}{y_{CO} y_{H_2O}} \quad (6)$$

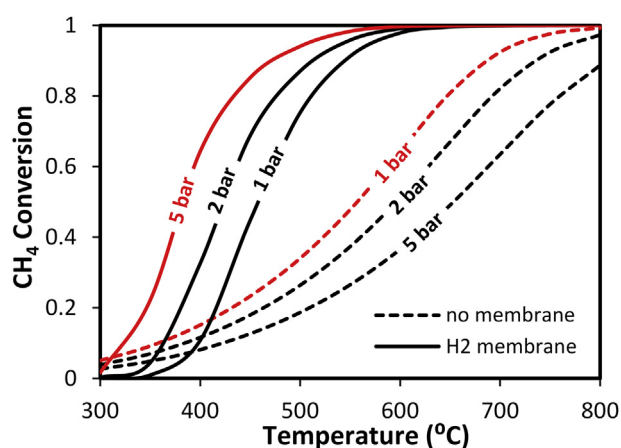


Fig. 1 – Equilibrium CH₄ conversion for a reactor with (solid lines) and without (dashed lines) a selectively permeable H₂ membrane at various operating pressures (assumed uniform within the reactor).

where the equilibrium constants for reverse methanation (K_1) and WGS (K_2) are calculated as function of the reaction temperature using empirical correlations [36]. Lastly, if a selectively permeable H_2 membrane is present, the final H_2 partial pressure in the reactor must be equal to the hydrogen partial pressure on the permeate side of the membrane ($P_{H_2,perm}$). In the case of no membrane, this constraint reduces to a vanishing rate of H_2 permeation, i.e.,

$$\begin{aligned} P_{H_2,perm} &= y_{H_2} \cdot P_{rxn} \text{ (with membrane)} \\ \text{or} \\ N_{H_2,perm} &= 0 \text{ (without membrane)} \end{aligned} \quad (7)$$

Impact of hydrogen removal via membrane separation on equilibrium conversion

Fig. 1 shows the equilibrium CH_4 conversion at various pressures as a function of temperature of an initially pure methane–steam mixture with S/C ratio of 2. For cases with a membrane, the H_2 partial pressure on the permeate side of the membrane is held constant at 0.2 bar by an inert sweep gas or consumption in an appropriate (electro)chemical device. Without a membrane, reaction temperatures in excess of 700 °C are required to achieve a conversion of greater than 90%, while the same can be achieved at less than 500 °C with a membrane reactor at 5 bar reaction pressure. Catalyst coking at these temperatures and a low S/C ratio is a potential issue that will be discussed further in the Results and discussion section.

It is important to note that without a membrane, conversion decreases with increasing pressure, as is expected from Le Chatelier's principle because an increasing number of moles result from the overall reaction. In contrast, with a membrane conversion increases with increasing pressure because of the additional removal of H_2 from the reaction chamber at higher pressures due to increased driving force for permeation across the membrane. This is important because it enables operation at higher pressure to increase the volumetric H_2 yield density without hurting the final achievable

CH_4 conversion. Also when coupled with CO_2 adsorption, as will be introduced in the Equilibrium conversion enhancement with CO_2 sorption section, operating at higher pressure with H_2 removal enables a higher CO_2 partial pressure and thus more favorable conditions for increased quantity of CO_2 adsorption. While increased reaction pressure is always favorable for equilibrium conversion with a membrane, the maximum pressure is limited by the mechanical strength of the membrane; for the purpose of this paper, this limit is arbitrarily set to be 5 bar.

At very low temperatures, the conversion without a membrane actually exceeds that of the membrane case. This is an artifact of setting the equilibrium hydrogen partial pressure on the retentate side to a fixed value equal to that of the permeate side. At low temperatures, so little hydrogen is produced by the chemical reactions that in order to satisfy Eq. (7), hydrogen from the retentate side must actually permeate into the reactor (i.e., $N_{H_2,perm} < 0$) to achieve equilibrium. The additional back-permeated hydrogen inhibits the equilibrium extent of the reactions and reduces the conversion as compared to the case without a membrane.

Equilibrium conversion enhancement with CO_2 sorption

Fig. 2 illustrates the supplemental increase in CH_4 conversion which can be achieved by incorporating CO_2 adsorption. Calculations are made at 5 bar pressure for the case with a membrane and 1 bar without a membrane, because each represents the highest possible conversion without sorption within the pressure range considered. For each case, methane conversion with removal (r) of 50% and 90% of the produced CO_2 is plotted. With 90% CO_2 removal and H_2 separation via membrane, it is possible to achieve 90% CH_4 conversion at temperatures below 400 °C. In contrast, without a membrane even removing a large fraction of the produced CO_2 does not result in conversions close to 90% in the temperature range considered (up to 600 °C).

Comparing the magnitude of conversion enhancement associated with CO_2 removal with and without a hydrogen permeable membrane, it is clear there is a synergistic effect in combining CO_2 sorption with H_2 removal. The use of a hydrogen membrane also appears to have a more significant impact on achievable conversion at a given temperature than CO_2 removal; this is to be expected because 3-to-4 molecules of H_2 are produced per molecule of CH_4 consumed while less than 1 molecule of CO_2 is produced (with the exact value of H_2 and CO_2 production depending on the extent of reverse methanation vs. WGS reaction). A key result of SMR thermodynamic equilibrium analysis is that both a hydrogen permeable membrane and CO_2 sorption are required for the CHAMP reactor to achieve a desirable conversion level (>90%) with methane as feedstock at temperatures as low as 400 °C.

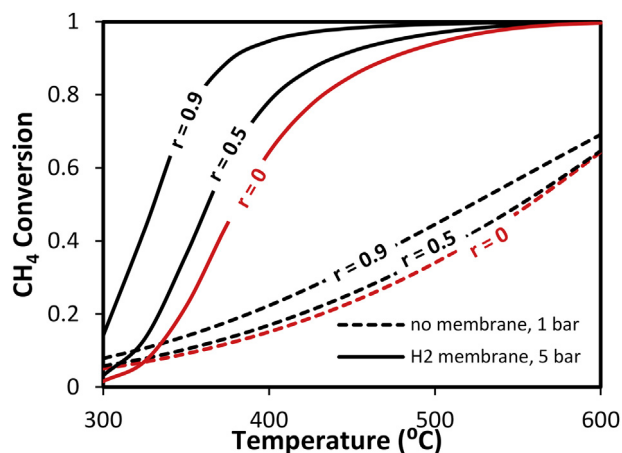


Fig. 2 – CH_4 conversion enhancement by removal of CO_2 via adsorption both with (solid lines) and without (dashed lines) hydrogen separation via a membrane.

CHAMP reactor with CO_2 sorption

The equilibrium calculations for sorption requirements in the CO_2/H_2 separation requirements for low temperature SMR section are general and made without consideration for how CO_2 is removed from the system or the type of reactor (batch

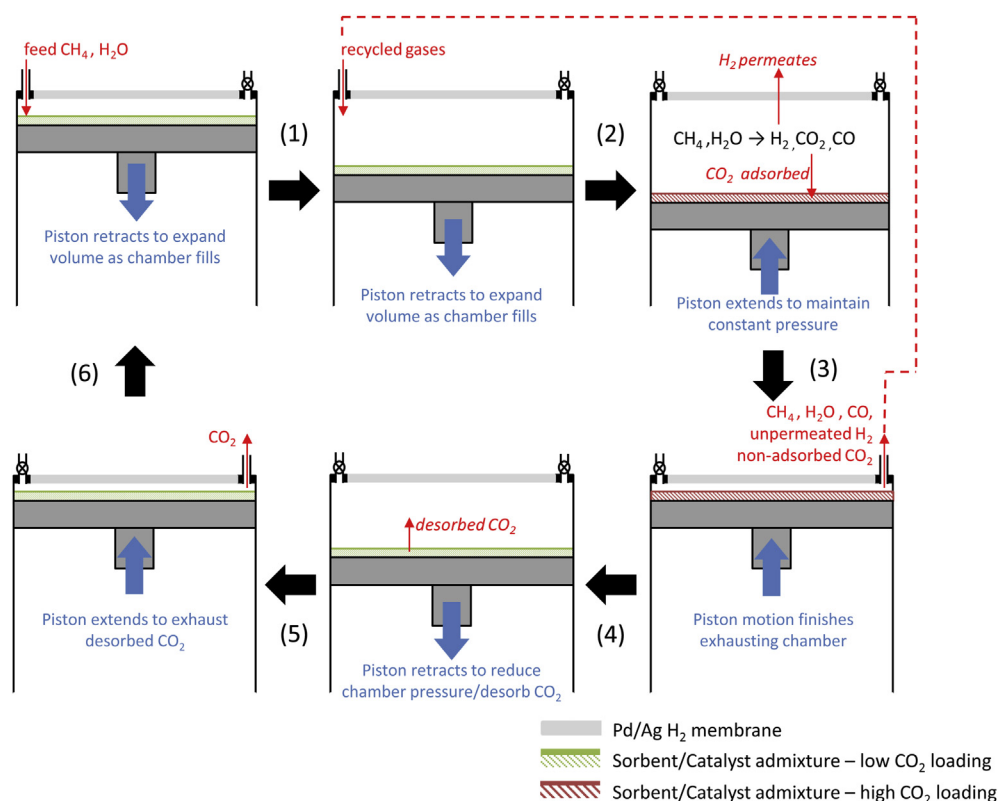


Fig. 3 – Schematic of CHAMP-SORB reactor cycle. The reactor utilizes four strokes per cycle: (6–1–2) retracting piston to fill the reactor, (2–3–4) extending piston to produce H_2 via SMR at constant pressure and then opening valve to exhaust products, (4–5) retracting piston to desorb CO_2 and (5–6) extending piston to desorb and produce a purified CO_2 as the final product.

or continuous flow). This section describes a particular embodiment of a modified CHAMP reactor, termed CHAMP-SORB, which can facilitate low temperature hydrogen production via SMR with selective CO_2 adsorption incorporated. It also discusses how the sorption isotherm's shape will impact the reactor performance and identifies the most appropriate sorbent option that matches with batch-mode operation of the CHAMP-SORB reactor.

CHAMP-SORB reactor process description

Fig. 3 illustrates the steps of the proposed cyclic CHAMP-SORB reactor with CO_2 adsorption. In contrast to the basic CHAMP embodiment [34], which utilizes only one intake and one reaction/exhaust stroke, the CHAMP-SORB reactor operates in a four-stroke cycle. Proceeding clockwise from top left in Fig. 3, the reactor is first filled with a mixture of CH_4 and H_2O , as well as recycled products from the previous cycle (if desired). The mixture then undergoes the steam–methane reforming reaction, which is enhanced by permeation of H_2 through the palladium–silver membrane and adsorption of CO_2 . During this step, the piston moves upwards to maintain constant pressure as selected species are removed from the gas phase via adsorption and permeation, and the temperature is maintained by heating the sorbent/catalyst admixture layer (not shown). After the SMR reaction has proceeded sufficiently, the exhaust valve opens and the upstroke is completed to fully exhaust the chamber. As denoted by the

dotted line, part or all of the exhaust gases can be recycled to the filling downstroke of the next CHAMP cycle if losses of residual hydrogen and unconverted methane upon exhaust are to be minimized. The Results and discussion section will show that this recycling has a positive impact on thermal efficiency of the reactor, but can come at a significant cost to volumetric H_2 yield density.

Once the chamber is exhausted, a second downstroke expands the chamber volume to reduce pressure and to facilitate desorption of CO_2 , with heat addition to maintain temperature during the endothermic desorption process. Lastly a second upstroke exhausts the desorbed CO_2 from the reaction chamber, allowing it to be captured if desired. Note that CO_2 may not be fully removed during the desorption step and this sorbent loading will then be carried over to the start of the subsequent cycle.

To model the cyclic performance of the CHAMP-SORB reactor, species conservation is solved at each of the states 1–6 labeled in Fig. 3. It is assumed that the reaction/permeation/adsorption and desorption steps both proceed fully to equilibrium and that sufficient heat is added to maintain isothermal conditions. It is also assumed that the filling processes 6–1–2 is fast enough that no CO_2 adsorption/desorption or SMR reaction occurs during this step. Similarly no change in sorbent loading is assumed to occur in the CO_2 exhaust step 5–6. Lastly, the system is modeled as if the chamber can be completely exhausted (i.e., neglecting any dead volume) at states 4 and 6 when the piston is fully

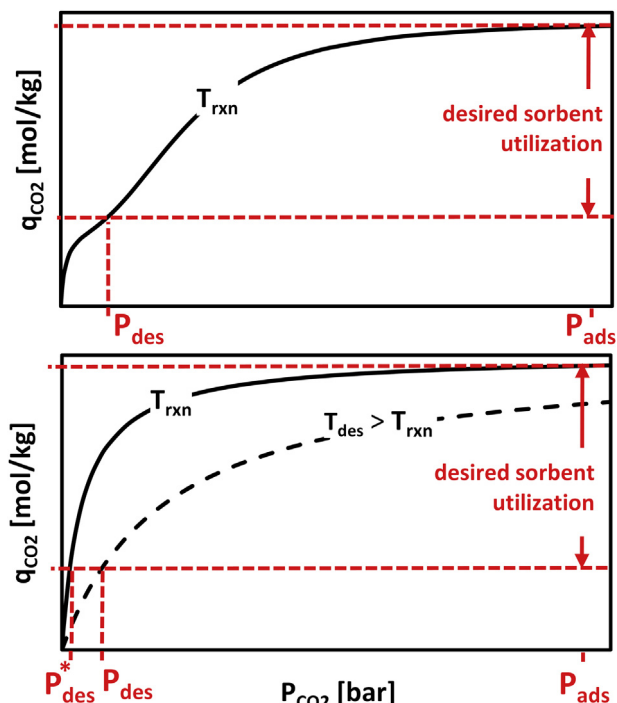


Fig. 4 – Illustration of impact of isotherm type on sorbent utilization and required reactor pressure and temperature. Type IV (top figure) isotherm allows a higher CO₂ pressure (P_{des}) during the desorption stage than the Type I (bottom figure) isotherm would require (P_{des}^*). The same desorption pressure can be achieved with the Type I isotherm only by incorporating a temperature swing between reaction and desorption.

extended and the top of the sorbent/catalyst admixture layer reaches the membrane; this assumption is valid with a thin layer of sorbent but as the sorbent volume increases the amount of gas contained within the sorbent void fraction may become significant.

In addition to solving the species balance, it is necessary to determine the required heat and work inputs for each step of the process to enable calculation of the overall thermal efficiency as a function of key process variables (temperature, pressure, S/C ratio, sorbent mass and recycle fraction). In doing so it is assumed that all expansion or compression steps are frictionless, quasi-equilibrium processes. The volume expansion during desorption step is assumed to occur slowly enough that the CO₂ loading of the sorbent remains in equilibrium with the surrounding gas. [Supplementary document S1](#) details the full set of equations and solution procedure for the species balance at each state 1–6, along with the required heat and boundary work inputs for each process.

Impact of sorption isotherm shape on CHAMP-SORB performance

Because the sorbent loading from a previous cycle is carried over to the next, the amount of CO₂ removed by adsorption during the reaction process 2–3 is equivalent to the amount

desorbed during the volume expansion process 4–5. This removed quantity of CO₂, $N_{CO_2,des}$, is equal to the mass of sorbent, m_{sorb} , multiplied by the difference in mass-based sorbent loading, q_{CO_2} , between state 3 (with high loading at “low” reaction temperature $T_3 = T_{rxn}$ and “high” adsorption pressure $P_3 = P_{ads}$) and state 5 (with low loading at “high” desorption temperature $T_5 = T_{des}$ and “low” desorption pressure $P_5 = P_{des}$).

$$N_{CO_2,des} = m_{sorb} [q_{CO_2}(T_{rxn}, P_{ads}) - q_{CO_2}(T_{des}, P_{des})] \quad (8)$$

The shape of the adsorption isotherm will then have significant impact on the achievable CO₂ removal and the effective sorbent utilization. To illustrate this impact, [Fig. 4](#) shows two isotherms with identical saturation capacity at high CO₂ pressure and the same slope in the low pressure Henry’s region at a given temperature. The bottom isotherm is a classic Type I Langmuir isotherm while the top isotherm is Type IV by Brunauer classification [37], with two inflection points and a concave up region at moderate pressure which is often used to represent a multi-layer adsorption behavior. To achieve a desired sorbent utilization under isothermal conditions, the pressure in the chamber for the Langmuir isotherm must be brought lower (P_{des}^*) than would be required for the sorbent with the Type IV isotherm (P_{des}). Alternatively, if the same desorption pressure (e.g., P_{des}) were desired for the Langmuir isotherm, combined temperature/pressure swing would have to be utilized ($T_{des} > T_{rxn}$) in order to achieve the same amount of CO₂ desorption.

Desorption pressure is critical for the cyclic CHAMP-SORB reactor, which relies on volume expansion alone to achieve the desired pressure swing. As such, the desorbed CO₂ remains in the reactor chamber, and the required expansion volume (state 5 in [Fig. 3](#)) is related to the CO₂ desorption pressure by the ideal gas equation of state:

$$P_{des} = \frac{N_{CO_2,des}RT}{V_5} \quad (9)$$

As the required desorption pressure to achieve a desired sorbent utilization goes to zero, the required desorption volume approaches infinity. For distributed applications where a small footprint is required, a realistic practical limit on the desorption volume is that it matches the maximum volume of the system when filled with fuel at state 2. Comparing the isotherms of [Fig. 4](#), a sorbent with a Type IV isotherm is preferred for the batch reactors such as CHAMP-SORB because it leads to a less stringent low pressure requirement for adequate desorption than would be required for a Type I isotherm sorbent.

Comparison between CHAMP-SORB and traditional SE-SMR with PSA regeneration

Because the utility of a sorbent is lost when it becomes saturated, sorption-enhanced (SE) reaction processes are inherently transient whether a variable volume batch or fixed bed flow arrangement is used. The traditional approach to SE-SMR employs at least two fixed bed reactor units operating out of phase, with one regenerating while the other is producing hydrogen. When PSA is used for sorbent regeneration, CO₂

desorption is accomplished by reducing reactor pressure below that of the reaction/adsorption step, followed by flushing the chamber with a purge gas and then repressurizing with a portion of the H_2 product gas. During the purge and repressurization step, the flow is in the reverse direction to that of the reaction/adsorption step to push the CO_2 sorbent loading front towards the entrance of the reactor, ensuring that essentially pure H_2 product (on a dry basis) occupies the reactor volume at the end of desorption/regeneration phase, which is then pushed out the reactor when the flow direction is again switched and the subsequent reaction step begins [38]. For applications where CO_2 sequestration is desired, steam has been proposed as the most suitable purge gas because it can be easily condensed out from the mixture; however it has been shown that an extremely high ratio of purge gas to desorbed CO_2 (greater than 60:1) is required to fully regenerate the sorbent [26]. A similar approach using temperature swing adsorption (TSA) at constant pressure as opposed to PSA has been proposed, but it still requires a significant amount of purge steam in a ~6:1 ratio with respect to H_2 product [11]. Accounting for the 1 to (3 or 4) ratio of CO_2 to H_2 produced by the overall SMR reaction, this equates to a roughly 20:1 ratio of purge gas to desorbed CO_2 . As explained in the Introduction section of this paper, this can be problematic for distributed and size-constrained applications where steam may be less readily available and its use would be detrimental from the reaction yield density prospective. Additionally, the energy required to generate steam in the ratios described above can dramatically lower the process energy efficiency.

The CHAMP-SORB offers additional benefits over the traditional SE-SMR process in that it does not require purge gas when desorbing the CO_2 . Because the catalyst/sorbent admixture only fills a small portion of the reactor, it is possible to exhaust most of the gas by moving the piston to a position corresponding to minimum reactor volume. The purity of the H_2 product is ensured by membrane separation, so small amounts of residual CH_4 , CO , and CO_2 carried over to a subsequent cycle are not an issue. The CHAMP-SORB does have a disadvantage, however, in that regeneration of the sorbent is limited by the presence of desorbed CO_2 in the reactor chamber. This limitation can be seen in the coupling of Eqs. (8) and (9): as the volume is expanded, more CO_2 is desorbed according to the adsorption isotherm, which in turn limits the reduction in chamber pressure associated with the expansion process. Because the desorbed CO_2 remains in the chamber it is not possible to fully regenerate the sorbent in the CHAMP-SORB reactor when the reactor volume at the end of expansion/desorption step, which is capped by the initial volume occupied by the feed gas during the intake step. This is in contrast to a traditional PSA process, where the desorbed CO_2 is continuously exhausted from the reactor with a non-adsorbing purge species, and it is possible to fully regenerate the sorbent with sufficient purge gas flow.

The regeneration behavior of the CHAMP-SORB reactor has an interesting impact on the level of mass-based sorbent utilization, defined as the difference in loading between the adsorption and desorption steps and illustrated in Fig. 4, as additional sorbent is incorporated in the reactor. If total reactor pressure is sufficiently high, the sorbent loading (per

unit mass of sorbent) at the end of the reaction/adsorption step, $q_{CO_2}(T_{rxn}, P_{ads})$, remains nearly constant, regardless of sorbent mass, because the CO_2 partial pressure is high enough to fully saturate the sorbent. When the piston is moved to the system's maximum volume state to induce desorption, as more sorbent is present more CO_2 will be released into the gas phase according to Eq. (8). This in turn means that, as indicated by Eq. (9), the CO_2 pressure at the end of the desorption step will be higher as more sorbent is added to the reactor. The CO_2 desorption pressure and sorbent loading at state 5, $q_{CO_2}(T_{des}, P_{des})$, are linked by the adsorption isotherm, with loading monotonically increasing with pressure regardless of whether the isotherm is Type I or IV. As such, higher CO_2 desorption pressure corresponds to higher sorbent loading at the end of the desorption step (less complete desorption per unit mass) and thus lower specific sorbent utilization. There is therefore a diminishing returns associated with increasing the sorbent mass, in that adding more sorbent results in a lower effective working capacity.

Selection of CO_2 sorbent

Having discussed the general impact of the sorption isotherm on the CHAMP-SORB performance, specific high temperature sorbents are now considered to determine the most appropriate option for this application based on the currently available materials as reported in the literature. In addition to the isotherm shape considerations, the sorbent must have sufficient CO_2 adsorption capacity at temperatures above 400 °C and selectively adsorb CO_2 in presence of other gases, in particular water vapor. The sorbent must also have relatively fast kinetics and cyclic stability over many adsorption/desorption cycles. Several review papers outline the various sorbent options for SMR, including calcium oxides, lithium zirconate and hydrotalcites [39,40]. Though possessing high CO_2 capacity, CaO has poor cyclic stability and is more suited for temperature swing adsorption, requiring high regeneration temperatures. Lithium zirconate similarly is more suited for TSA, and it also suffers from relatively slow kinetics which is not considered in this paper but is an important consideration. Hydrotalcites have lower CO_2 capacities than the other options, but they are well suited for PSA and have excellent cyclic stability and adequate kinetics in the 400–600 °C temperature range.

The CO_2 adsorption properties of hydrotalcite-like compounds are sensitive to their preparation, in particular the Mg/Al ratio and degree of impregnation with alkali metals such as potassium or cesium carbonate [41]. Because the capacity is specific to the preparation method, many studies have reported variations in sorption capacity and other characteristics [31,42–46]. Of these, only one measured the sorption isotherm beyond a CO_2 pressure of 1 bar, most likely because higher CO_2 pressures are not relevant to conventional flow-through SMR reactors. However, data in this pressure range is critical for the CHAMP-SORB reactor, which can achieve high CO_2 partial pressure conditions as the CH_4 and H_2O are depleted by the SMR reaction and H_2 is removed from the reaction chamber via membrane permeation. The sorption isotherm reported by Lee et al. contains data up to 3 bar and is of Type IV, owing to a proposed mechanism which combines

monolayer adsorption with a multi-layer chemical complexation reaction [43]. Because it contains data at the required high CO_2 partial pressures, this isotherm is utilized in the CHAMP-SORB cyclic calculations that are reported next in the [Results and discussion](#) section.

Results and discussion

As outlined in the introduction, two key performance metrics for a small-scale distributed reactor, such as the CHAMP-SORB, are thermal (energy) efficiency and volumetric yield density. The thermal efficiency calculation is based on the ratio of heating values of the H_2 product to the CH_4 fuel, with the required heat and work inputs during all stages of the CHAMP-SORB cycle also accounted for (note that all calculations follow a sign convention that the work input is negative):

$$\eta_{\text{th}} = \frac{\text{LHV}_{\text{H}_2} \cdot N_{\text{H}_2, \text{perm}}}{\text{LHV}_{\text{CH}_4} \cdot N_{\text{CH}_4, 1} + \sum Q_{\text{in}} - W_{\text{b, out}}} \quad (10)$$

The energy required to increase the temperature and pressure of the initial mixture of liquid H_2O and gaseous CH_4 from a standard state (25 °C, 1 bar) to the elevated reaction temperature and pressure are included in the heat and work components of Eq. (10) [47]. The energy penalty associating with generating steam can become a significant factor in the overall thermal efficiency of the process, as the enthalpy of vaporization of one mole of liquid water at STP is *ca.* 20% of the endothermic heat of the reverse methanation reaction for one mole of CH_4 [26].

The hydrogen yield density is defined as the amount of H_2 permeated through the membrane in a given cycle divided by the maximum volume of the system. The maximum volume occurs at state 2 in Fig. 3, because the reactor contains the largest amount of gas species at this point (as discussed in the [CHAMP-SORB reactor process description](#) section, the final volume of the low pressure desorption step is constrained to match this volume). Both the volume of gas and the solid volume of the sorbent are included when determining the maximum volume for the yield density calculation:

$$V_{\text{max}} = V_2 = \sum_j N_{j,2} v_{j,2}(T_{\text{rxn}}, P_{\text{rxn}}) + (1 - \epsilon_t) \cdot m_{\text{sorb}} / \rho_{\text{sorb}} \quad (11)$$

where ϵ_t is the total porosity and ρ_{sorb} is the density of the hydrotalcite sorbent taken from Ding and Alpay [42], and $v_{j,2}$ is the specific volume of species j at the reaction (state 2) temperature and pressure.

Two additional metrics that are considered in assessing the CHAMP-SORB performance are hydrogen yield efficiency and CH_4 conversion. The yield efficiency is defined as the actual amount of H_2 permeated through the reactor divided by the maximum possible H_2 yield if all the carbon in the introduced CH_4 were oxidized to CO_2 (as opposed to some CO), which according to the stoichiometry of Eq. (3) is four times the number of moles of CH_4 fed. The CH_4 conversion is defined in a traditional sense of moles reacted divided by moles fed; however, it is important to note that when part of the exhaust gas mixture from the previous cycle is recycled, the moles of CH_4 fed only includes the quantity of new fuel that is added ($N_{\text{CH}_4, 1}$), not the total moles of fuel present after recycle

($N_{\text{CH}_4, 2}$). As a result, the general expression for CH_4 conversion is:

$$X_{\text{CH}_4} = \frac{N_{\text{CH}_4, 2} - N_{\text{CH}_4, 3}}{N_{\text{CH}_4, 1}} \quad (12)$$

CHAMP-SORB performance without fuel recycling

The first case considered is for baseline operation with no exhaust gas recirculation (recycling) from the previous cycle. If this is the case, states 1 and 2 in Fig. 3 are identical ($N_{j,1} = N_{j,2}$). Fig. 5 is a representative plot that shows how the thermal efficiency, hydrogen yield density, yield efficiency and conversion vary with S/C ratio at a fixed reaction temperature, pressure and mass of sorbent.

As expected from the Le Chatelier's principle, operating with more steam has a favorable impact on CH_4 conversion. Conversion monotonically increases with S/C ratio, an effect that is particularly pronounced for S/C ratios less than 3. Yield efficiency, however, trends closely with CH_4 conversion at low S/C ratios but reaches a maximum and actually tails off at S/C ratios greater than 4. This is due to a dilution effect of excess steam in the reactor chamber: even as more H_2 is produced at higher levels of CH_4 conversion, the hydrogen partial pressure is reduced due to an accumulation of non-permeating, non-adsorbing species in the chamber such that the additional H_2 cannot permeate out of the reactor. The dilution effect at high S/C ratios has a more pronounced effect on the hydrogen yield density due an extra volume required for additional steam in the feed, with yield density tailing off significantly with additional steam above an S/C ratio of 2. Operating at low S/C ratios, where H_2O becomes the limiting reactant, is also detrimental to yield density. As such, the optimal S/C ratio for hydrogen yield density is approximately 2, which corresponds to the stoichiometry of the combined SMR reaction given by Eq. (3).

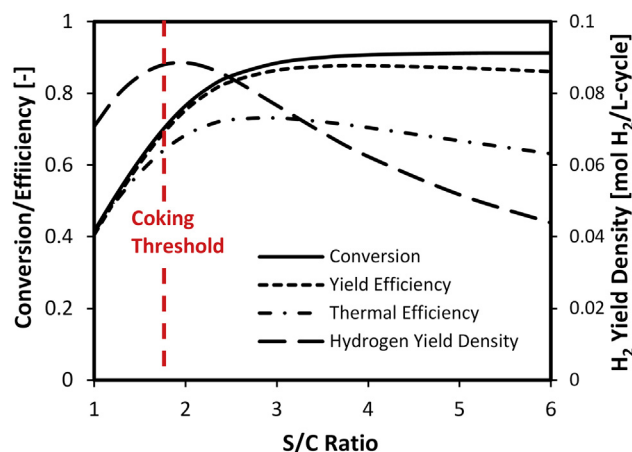


Fig. 5 – Impact of S/C ratio on conversion, yield efficiency, thermal efficiency and hydrogen yield density of CHAMP-SORB reactor. Calculations made with a sorbent mass of 1 kg/(initial mol CH_4) at 400 °C without any fuel regeneration.

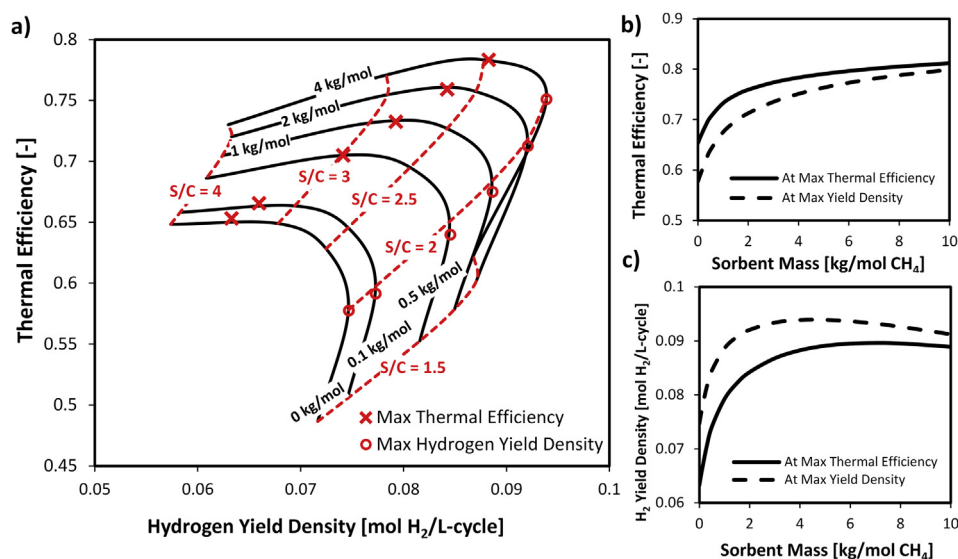


Fig. 6 – CHAMP-SORB reactor cyclic performance without regeneration: (a) Regime map for thermal efficiency versus cyclic hydrogen yield density at varying S/C ratios (---) and sorbent mass (—); (b) Thermal efficiency and (c) Hydrogen yield density as a function of sorbent loading with S/C ratios chosen to maximize each metric.

Determining the optimal S/C ratio for maximum thermal efficiency is not as straightforward as matching the stoichiometry of the combined SMR reaction for maximum yield density. The increase in conversion/yield efficiency with excess steam and the energetic penalty associated with generating steam are competing factors which lead to a maximum thermal efficiency at an S/C ratio of 2.8 for the conditions of Fig. 5. Below this optimal S/C ratio, operating with additional steam is favorable because the lower heating value of the extra H₂ produced outweighs the extra energy input required to produce the steam. Operating above the optimal S/C ratio, however, decreases the overall cycle's thermal efficiency as the energetic cost of producing steam becomes dominant. The tail off in thermal efficiency at higher than optimal S/C ratios is mitigated by the fact that the CH₄ conversion continues to increase, albeit at slower rates, with increased steam. As a result, the thermal efficiency penalty at high S/C ratios is not as pronounced as the reduction in hydrogen yield density.

Because the CHAMP-SORB reactor thermal efficiency and H₂ yield density analysis shows favorable operation at lower S/C ratios than typically found in industrial or sorption-enhanced SMR applications, it is important to consider the potential issue of catalyst deactivation through carbon deposition [48]. Carbon deposition on a catalyst can occur at high temperatures through the endothermic decomposition of methane ($\text{CH}_4 \rightleftharpoons \text{C} + 2\text{H}_2$) and at lower temperatures by the exothermic Boudouard reaction ($2\text{CO} \rightleftharpoons \text{C} + \text{CO}_2$) [49]. Methane decomposition is not likely at the lower CHAMP-SORB operating temperatures, but the possibility of low temperature carbon deposition through the Boudouard reaction is possible and more likely to occur at lower S/C ratios [25]. Snoeck et al. experimentally determined an expression for the “coking threshold” (i.e., the ratio of CO₂ to CO concentrations above which the net rate of carbon formation becomes zero) on a Ni steam reforming catalyst which can be used to

determine a critical S/C ratio below which there will be a risk of catalyst deactivation through coking [50]. For the conditions of Fig. 5, this coking threshold corresponds to an S/C ratio of 1.75. This result suggests that it is possible to operate the CHAMP-SORB at S/C ratios low enough to optimize H₂ yield density without risking coking of the catalyst, however it is important to recognize that the actual coking threshold will depend on the catalyst and should be monitored in any future experiments with a CHAMP-SORB class reactor. While an S/C coking threshold of 1.75 is specific to the conditions of Fig. 5, this parameter is monitored during all calculations presented in the following sections and is determined to be sufficiently low in all of these cases to not be a limiting factor in optimization.

Fig. 6 summarizes the simultaneous impact of varying the S/C ratio and amount of sorbent on the two key performance metrics, thermal efficiency and hydrogen yield density, at a temperature of 400 °C and pressure of 5 bar. The solid curves in Fig. 6(a) indicate lines of constant sorbent mass (per mole of CH₄ fed), while dashed curves are lines of constant S/C ratio. The same trend is seen as in Fig. 5, with increasing thermal efficiency and yield density at S/C ratios less than 2, followed by a region of decreasing yield density but increasing thermal efficiency at intermediate S/C ratios, and finally decreasing both the yield density and thermal efficiency at high S/C ratios. It can also be seen in Fig. 6(a) that the S/C ratio corresponding to maximum yield density (marked by circles in the plot) always occurs at or just slightly below 2 regardless of sorbent amount. This is in contrast to the S/C ratio corresponding to maximum thermal efficiency (marked by crosses), which decreases with increasing sorbent amount because the increased capacity to selectively remove CO₂ reduces the amount of required excess steam to enhance the conversion. The diminishing returns associated with including additional sorbent, the reasons for which were discussed in the Comparison between CHAMP-SORB and

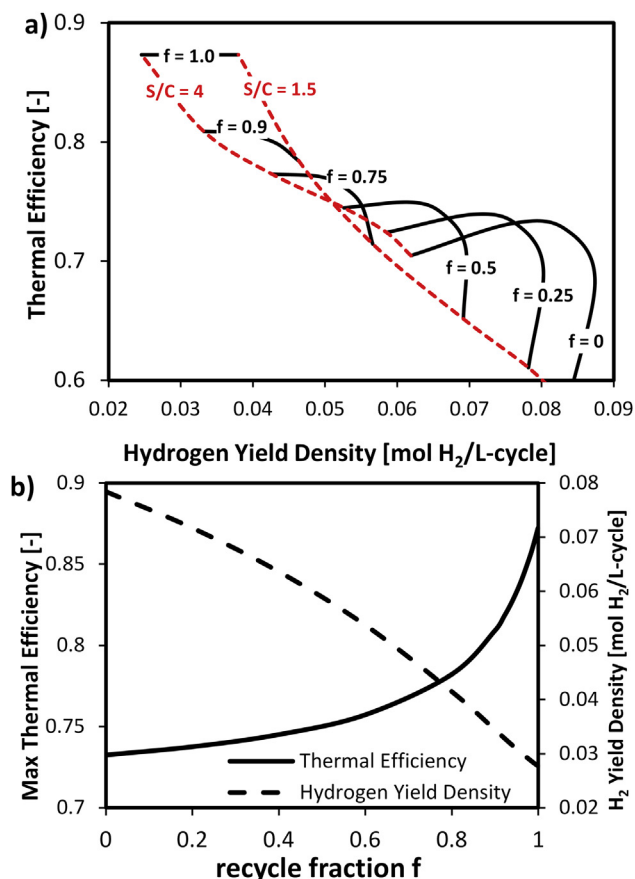


Fig. 7 – Impact of recycle fraction on CHAMP-SORB reactor thermal efficiency and hydrogen yield density: (a) Regime map for 1 kg sorbent/mol CH₄; (b) Maximum thermal efficiency with optimal S/C ratio as a function of recycle fraction and corresponding yield density tradeoff.

traditional SE-SMR with PSA regeneration section, can also be seen in Fig. 6(b) and (c), as increasingly more sorbent is required to provide the same benefit in thermal efficiency and yield density. The thermal efficiency and yield density both increase with additional sorbent at low sorbent levels; however, at very high sorbent amounts (greater than 4 kg/mol CH₄), the yield density can actually decrease with increasing sorbent mass. This occurs specifically at low S/C ratios and is due to the fact that the volume occupied by the sorbent becomes significant relative to the volume of gas in the reactor.

For each specific sorbent mass, the point corresponding to maximum thermal efficiency is labeled with an “x” and maximum yield density with an “o.” The loci of these points are plotted on Fig. 6(b) and (c), illustrating the impact of optimizing S/C ratio for thermal efficiency versus hydrogen yield density on each of these parameters, with additional data included beyond 4 kg/mol of sorbent. While Fig. 6(b) shows that thermal efficiency continues to monotonically increase with increasing amount of sorbent, according to Fig. 6(c) hydrogen yield density eventually tails off at high sorbent loadings regardless of whether the S/C ratio is chosen to maximize thermal efficiency or yield density.

CHAMP-SORB reactor performance with fuel recycling

At the end of the reaction/permeation/adsorption step, the residual gas in the reactor consists of some unreacted CH₄ as well as trace CO and unpermeated H₂. All of these are valuable, energy-carrying products, and because most of the hydrogen product is already separated from this mixture it is possible to recycle the residual gas from the CHAMP-SORB reactor exhaust to improve fuel utilization. To model this “closed-loop” mode of operation with product recycling, a recycle fraction (f), defined as the percentage of gas at the end of the reaction step that is recycled ($N_{j,2} = N_{j,1} + fN_{j,3}$), is introduced. The recycle fraction can take values between zero (no recycle) and unity (full recycle). In the case of full recycle, the reactor fully converts all CH₄ and H₂O introduced and outputs pure H₂ during the reaction step and pure CO₂ when the chamber is exhausted after the desorption step, resulting in a “closed-loop” operation.

Fig. 7 illustrates the impact of increasing the recycle fraction for a CHAMP-SORB cycle at 400 °C, 5 bar with a specific sorbent mass of 1 kg/mol CH₄ while changing the S/C ratio. The thermal efficiency versus hydrogen yield density curve for $f = 0$ in Fig. 7(a) matches its counterpart in Fig. 6(a), but as the recycle fraction is increased the curves gradually flatten out. The reason for this flattening is that the impact of lower conversion and hydrogen yield on thermal efficiency penalty at low S/C ratios is “softened” due to recycling of unconverted CH₄, as opposed to wasting it by exhausting without recycle. Similarly, the drop off in thermal efficiency at high S/C ratios is less severe with fuel recycling because a portion of the excess steam is carried over from the previous cycle and less energy of vaporization is required to generate new steam. As the regeneration fraction is increased from 0 to 1, the general trend is that thermal efficiency increases while hydrogen yield density decreases due to the added volume occupied by the recycled gas and carried over through the cycle. This tradeoff is further illustrated in Fig. 7(b), which depicts thermal efficiency and corresponding hydrogen yield density as a function of recycle fraction where at all points the S/C ratio is chosen to optimize efficiency.

When the full amount of residual gas is carried over to the next cycle (i.e., $f = 1.0$), the thermal efficiency becomes a constant value regardless of S/C ratio. This result can be understood by recognizing that the amount of gaseous CO₂, CO and H₂ must be equal at the beginning and end of the reaction/permeation/adsorption step (states 2 and 3, respectively, in Fig. 3) during cyclic operation because only CH₄ and H₂O are added to the reactor from one cycle to the next. To keep the CO quantity constant, the reverse methanation and WGS reactions must proceed to equal extents because carbon monoxide is neither permeated nor adsorbed out from the reaction chamber. As such, the net overall reaction must match that of Eq. (3), and therefore all the CO₂ and H₂ produced must be removed from the gas phase by adsorption and permeation, respectively, for their quantities to remain equivalent from state 2 to 3. Ultimately, this fixes the proportion of permeated H₂ to added (new fuel increment) CH₄ (4:1) and H₂O (2:1) for each CHAMP-SORB cycle, regardless of the operating S/C ratio after the recycled gas is introduced to the chamber at the start

of the reaction/permeation/adsorption step. As a result, the thermal efficiency approaches a fixed value with full regeneration, as the heating value of CH_4 along with the heat required to preheat the fuel and maintain isothermal conditions during cyclic operation are always held in fixed proportion relative to the heating value of H_2 that is permeated from the reactor.

The reasoning above holds true regardless of sorbent mass, so it is expected that this constant thermal efficiency with full regeneration should remain unchanged with varying sorbent amount at a given reaction temperature and pressure. This is confirmed by the results in Fig. 8, which is a regime map of thermal efficiency versus hydrogen yield density for varying the sorbent mass and recycle fraction (with the S/C ratio implicitly varied at each data point to maximize thermal efficiency). The curve for 100% recycle is not plotted because the optimal S/C ratio for maximum thermal efficiency is arbitrary when the efficiency is constant, but the curve for 99.9% shows that the thermal efficiency reaches a constant value equal to that of Fig. 7(a) for all non-zero sorbent amounts.

Moving along lines of constant recycle fraction in Fig. 8, an increase in the sorbent amount increases both thermal efficiency and hydrogen yield density until the volume occupied by the sorbent becomes significant relative to the gas volume of the reactor chamber. Beyond this point additional sorbent continues to increase thermal efficiency while hurting yield density, in agreement with previously observed trends. The sorbent mass at which hydrogen yield density is negatively impacted does grow, however, with increasing recycle fraction because the added volume of the recycled gases delays the deleterious effect of solid volume occupied by the sorbent. Another important result of Fig. 8 is that the thermal efficiency's benefit of exhaust recycling is only present when

there is some non-vanishing amount of sorbent. This is because without a sorbent to perturb the equilibrium state of the recycled gases, there is no conversion enhancement associated with recycling. Therefore, adding an increasing amount of exhaust gas in the absence of a sorbent only serves to decrease the hydrogen yield density while keeping thermal efficiency constant. Lastly, as more sorbent is added to the reactor an increasingly smaller fraction of residual products needs to be recycled in order to achieve the same thermal efficiency, while the associated hydrogen yield density penalty becomes lessened.

Conclusions

A new class of variable volume batch-membrane reactor with integrated CO_2 sorption, termed CHAMP-SORB, is introduced to produce hydrogen from methane feedstock with consideration given to constraints imposed by distributed applications if natural gas is used as a primary source of methane. It is shown that both H_2 and CO_2 separation is required to be able to achieve desirable conversion levels at temperatures as low as 400°C with low S/C ratios, which are desirable for greater thermal efficiency and hydrogen yield density. The CHAMP-SORB reactor has advantages over traditional SE-SMR approaches in that it does not require a purge gas for sorbent regeneration and is more scalable to different hydrogen generation demands; however this comes with a constraint on maximum achievable sorbent utilization because the desorbed CO_2 remains in the reactor as the volume is expanded rather than is continuously purged as is in the case of continuous flow SE-SME reactors. A “closed-loop” mode of the CHAMP-SORB reactor operation with partial or full recycle of unreacted reaction products with recoverable energy content is introduced, which allows one to maximize thermal efficiency and provides a compelling option for applications involving CO_2 capture combined with power (H_2) generation.

Regime maps for the reactor quasi-equilibrium operation of the CHAMP-SORB reactor, with and without product recycle, are reported which explore the tradeoff between thermal efficiency and hydrogen yield density at a given temperature and pressure, as a function of sorbent mass, S/C ratio and recycle fraction. The analysis yielded the following fundamental insights and recommendations:

- The optimal S/C ratio in the feed that maximizes hydrogen yield density is approximately 2 regardless of sorbent mass. S/C ratios above 2 are desired for maximum thermal efficiency; however, with increasing sorbent mass less excess steam is required for optimal thermal efficiency because of the incremental equilibrium shift provided by the additional CO_2 sorption.
- There is a diminishing return on sorbent utilization and CH_4 conversion enhancement as more sorbent is added due to the nature of sorbent regeneration into a fixed volume environment of the batch reactor without use of an inert carrier gas. Further, initially increasing the sorbent amount increases both thermal efficiency and yield density of the variable volume batch reactor, but eventually yield density suffers when the fraction of reactor volume

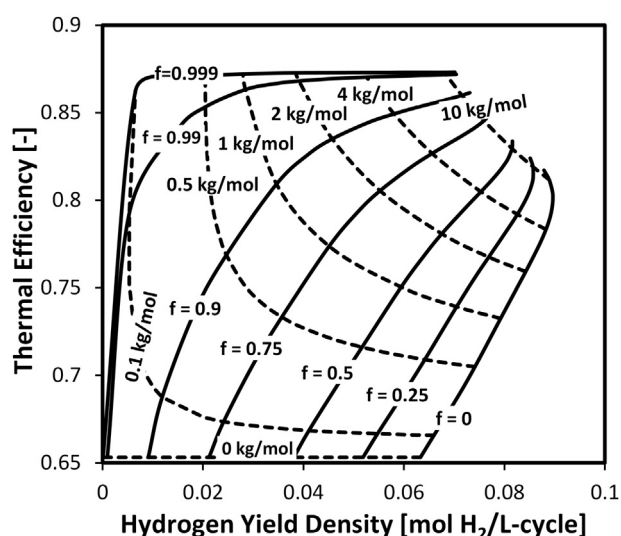


Fig. 8 – Regime map for CHAMP-SORB cyclic performance with exhaust recycling (all results are for different S/C ratios chosen to maximize thermal efficiency at each recycle fraction and sorbent mass combinations). Dashed lines represent foci of constant sorbent mass (per unit of added fuel) while solid lines represent foci of constant recycle fraction.

occupied by adsorbent becomes significant relative to the gas volume.

- Increasing “degree of recycling”, i.e., the fraction of unreacted reactants and un-separated products at the end of each cycle that is fed back to the reactor for the next consecutive cycle, increases thermal efficiency of the process up to its maximum at 100% recycling, but there is an associated reduction in hydrogen yield density due to a carry-over volume associated with the recycled, rather than simply exhausted, product stream. Importantly, the improvement in process thermal efficiency is not only due to mitigation of a waste of unreacted fuel especially at low S/C ratios, but also owes to a decrease in the energy input required for extra steam production especially at high S/C ratios when the fuel conversion is intrinsically high.
- The thermal efficiency benefit of incorporating recycling is only present when CO₂ sorption is incorporated into the CHAMP reactor operation. As more sorbent is added, a lesser degree of recycling is required to achieve a desired level of thermal efficiency, albeit at the expense of simultaneous reduction in hydrogen yield density.
- As a the recycle fraction approaches unity, the thermal efficiency converges to a constant value, irrespective of either the sorbent mass or post-recycle S/C ratio, because H₂ and CO₂ are produced in a fixed proportion relative to the consumed CH₄ and H₂O.

The thermodynamic analysis in this paper shows that CHAMP-SORB cycle is a viable option for low temperature distributed production of hydrogen via sorption-enhanced steam methane reforming, and establishes a thermodynamic envelope for ideal reactor performance. In particular, the CHAMP-SORB is envisioned as a promising option for stationary forecourt hydrogen production at the point of fuel cell vehicle refueling or for residential fuel cell applications; however, it could also prove viable for larger scale mobile transport applications (e.g. interstate trucks, trains, etc.). With inclusion of reaction kinetics and heat/mass transfer effects, a comprehensive analytical methodology for the CHAMP-SORB class of reactors should allow determination of practically-relevant performance characteristics, such as hydrogen yield density, reactor throughput and scalability, to further assess the application potential of this new fuel processing approach. With regards to overall CHAMP-SORB system cost as compared to a more conventional SMR process with low temperature WGS and PSA, several factors will be important. Operation at lower temperature and elimination of the components required for the WGS and PSA steps will reduce cost of the CHAMP-SORB, however the additional cost of an infinitely selective palladium-based membrane must be considered. Looking forward, the CHAMP-SORB may be able to utilize alternative lower-cost membranes with suitable hydrogen permeability and selectivity as they are developed.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.ijhydene.2014.03.127>.

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